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Researches in the Acenaphthene Field



DISSERTATION

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By

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RESEARCHES IN THE ACENAPHTHENE FIELD

ABSTRACT

This investigation was undertaken with the intention of extending to acenaphthene the study of the peri-metathiazines. For this purpose 4,3-nitroacenaphthenesulfonyl chloride was desired as a starting material. As soon as the preparation of this compound was investigated, it became evident that the structures of the monosulfonic acids of acenaphthene had been the subject of considerable conflicting research. Therefore, it seemed highly desirable to obtain a simple and straightforward proof of structure for 3-acenaphthenesulfonic acid. It also became evident that practically no work had been done on the proof of the position of the nitro group in 4,3-nitroacenaphthenesulfonic acid. Hence this latter problem of structures was first attacked, and on its completion, the desired peri-acenaphthothiazines were prepared.

In carrying out the above purposes, the following procedure was used:

Acenaphthene was nitrated at low temperature, and the nitro group was then reduced to an amino group. The amine was converted to a sulfonic acid which was found to be identical with the sulfonic acid that was obtained by direct low temperature sulfonation of acenaphthene.

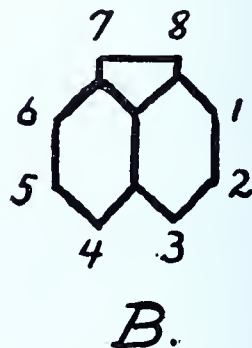
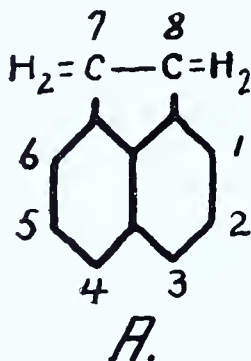
The sodium 3-acenaphthenesulfonate and its acid chloride were nitrated. Sodium 4,3-nitroacenaphthenesulfonate and 4,3-nitroacenaphthenesulfonyl chloride were isolated; and these on reduction and removal of the sulfonic group and sulfonylchloride group respectively, gave 3-aminoacenaphthene. The 4,3-aminoacenaphthenesulfonic acid was converted to a sultone.

The 4,3-nitroacenaphthenesulfonyl chloride was reduced to the chlorostannate of the peri-aminoacenaphthenyl mercaptan from which a series of condensation products was prepared.

The 2-(p-aminophenyl) and 2-(m-aminophenyl)-peri-acenaphthothiazines were converted to dyes of the Columbia Yellow type.

Nomenclature

The system of nomenclature used in this dissertation is that of Chemical Abstracts. It is illustrated by Figure A. For simplicity on the flow sheets it has been drawn as illustrated by Figure B. Positions 3 and 4 have been called peri positions.



Seven systems of naming acenaphthene compounds have been encountered in the course of investigating the literature. The naming has been changed wherever necessary so that all names are given according to the system of Chemical Abstracts.

HISTORICAL AND DISCUSSION

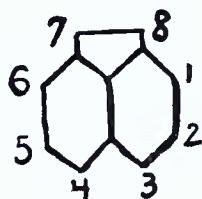
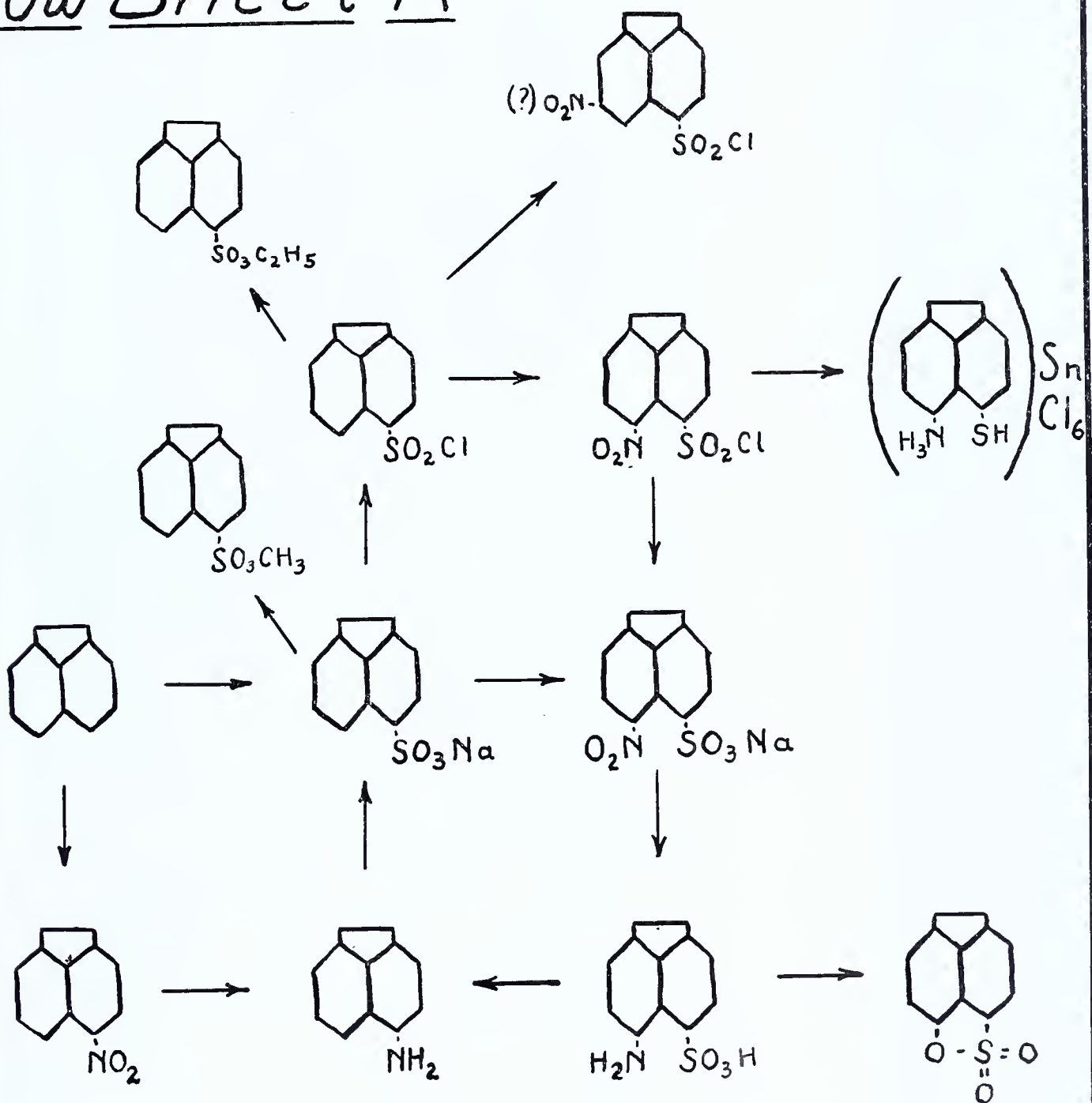
Structure in the Acenaphthene Field

3-nitroacenaphthene

Much of the proof of structure in the acenaphthene field has been based upon the position of the nitro group which enters the hydrocarbon when it is nitrated at low temperature ($10-18^{\circ}$) in acetic acid solution. The position of this nitro group has been used as a starting point for the proofs presented in this dissertation.

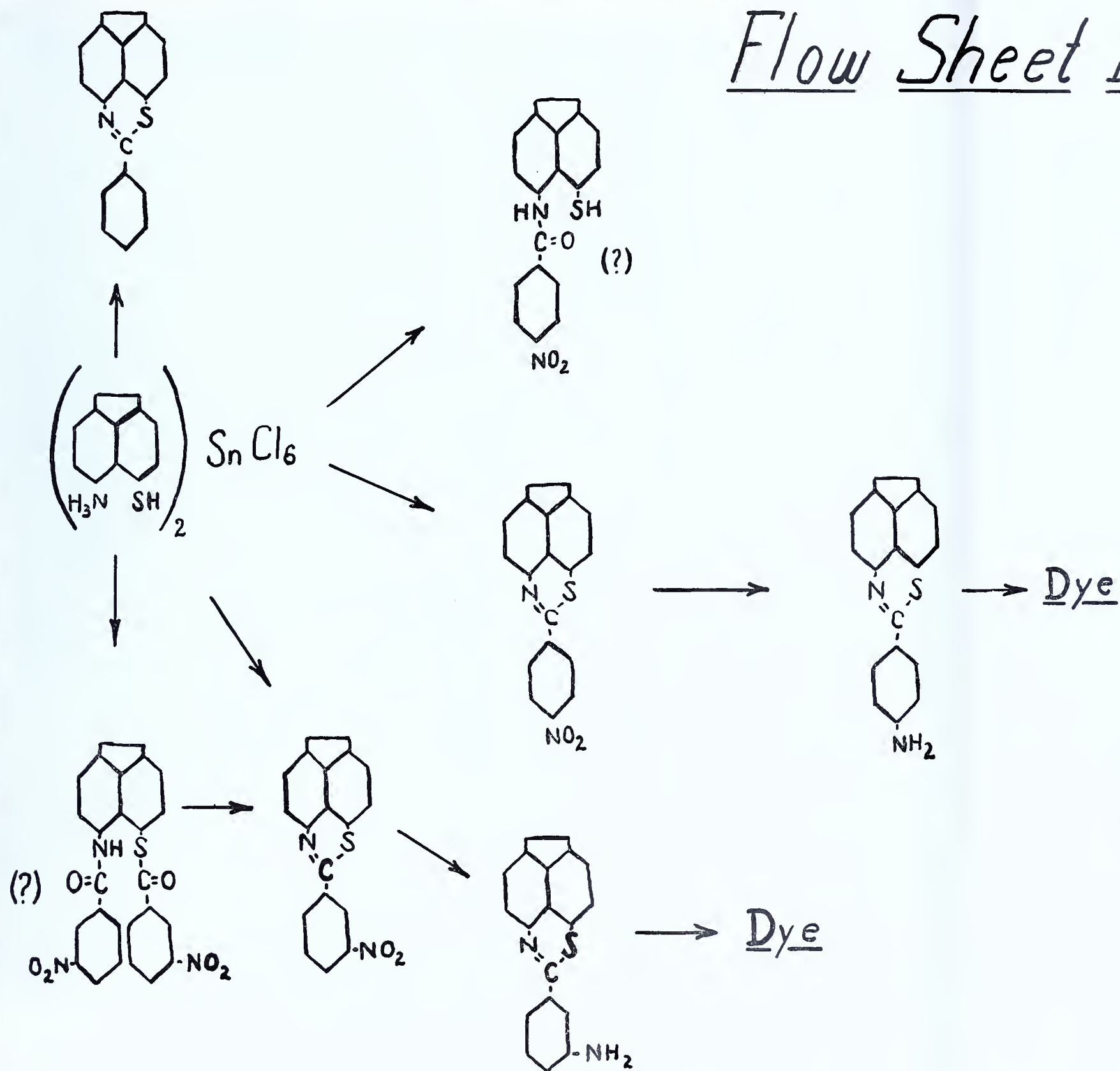
Blumenthal ¹ in 1874 used oxidation of the methylene groups to determine whether substitution had taken place on these groups or on the aromatic nucleus. Graebe and Briones ¹¹ extended this method, and used it as a proof of the position of the nitro group in 3-nitroacenaphthene. The reactions used by them are illustrated on flow-sheet C as No. 1. By nitrating the hydrocarbon in acetic acid, oxidizing the product with potassium dichromate to a nitronaphthalic acid, reducing to the amino acid, and distilling the sodium salt of the latter with calcium hydroxide, alpha naphthylamine was obtained. Therefore, the original nitro compound was considered to be 3-nitroacenaphthene, positions 3 and 4 being the same, of course, when no other group is present.

Flow Sheet A

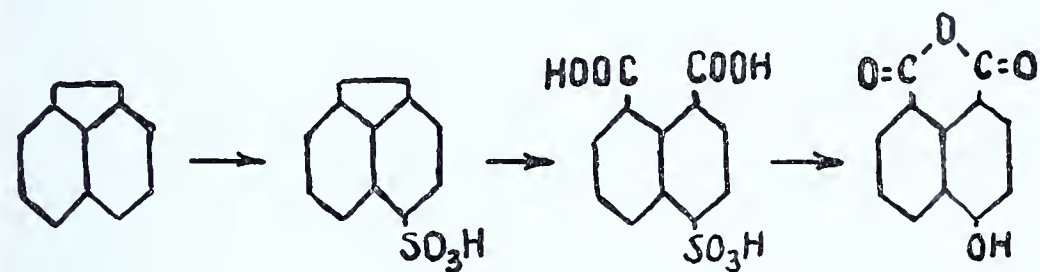
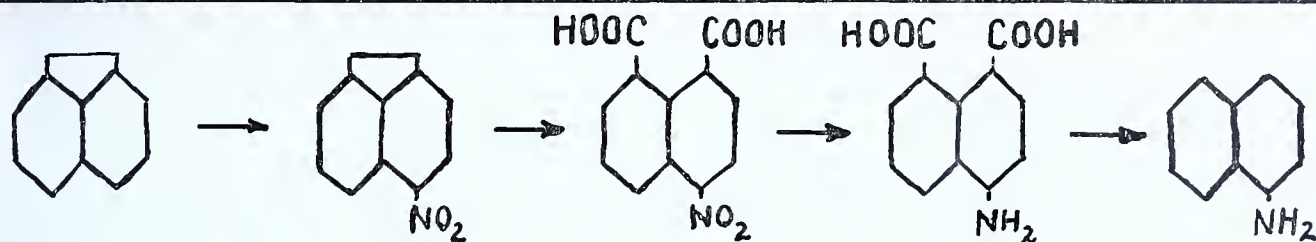


3 and 4 are also "peri"

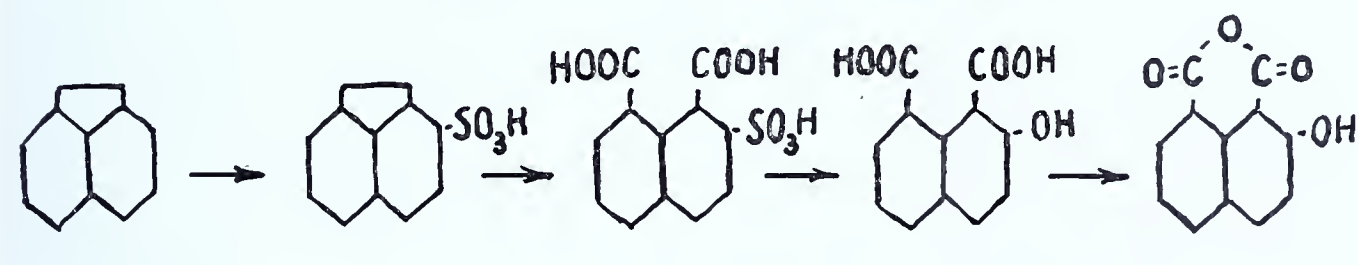
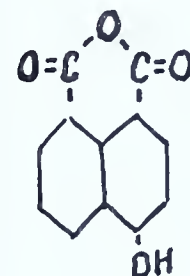
Flow Sheet B



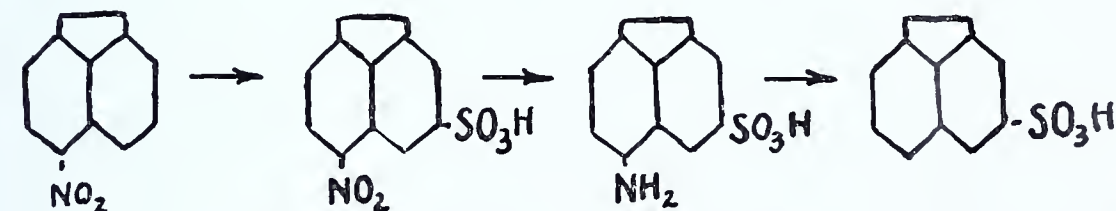
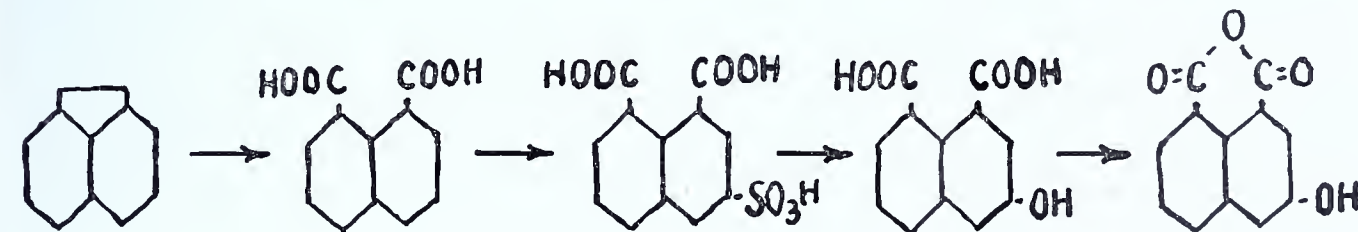
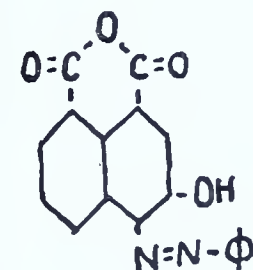
Flow Sheet C



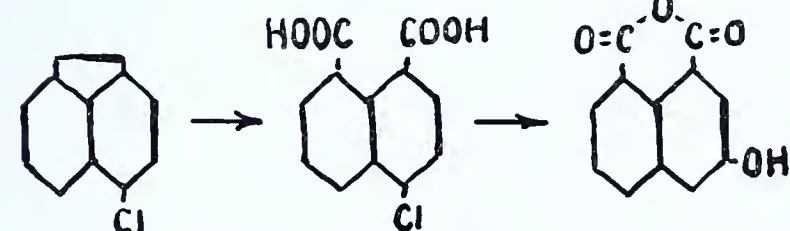
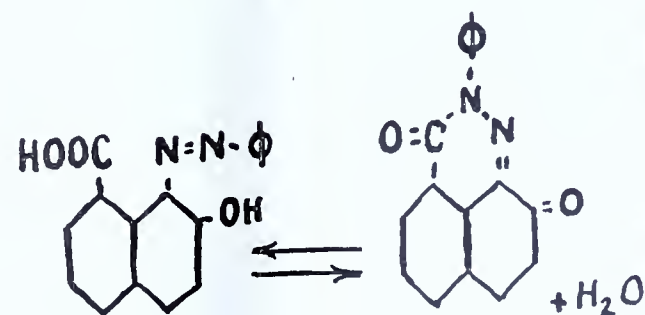
II



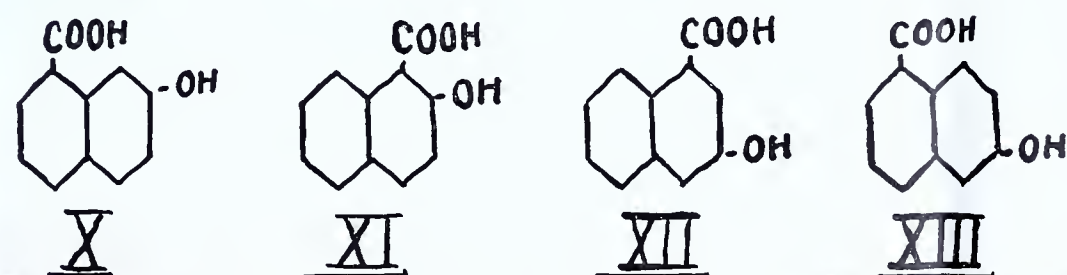
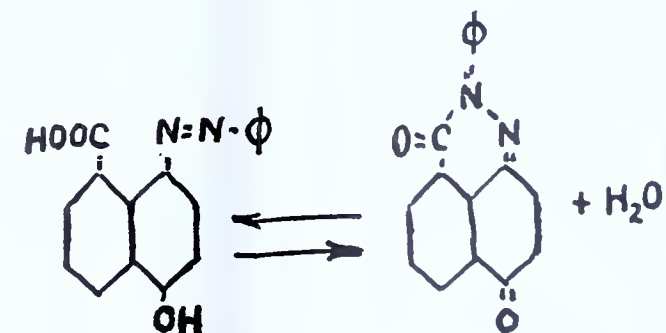
VI



VII



VIII



A check on the position of this nitro group has been obtained in the course of this work. It will be discussed after the presentation of the history of the three acenaphthenesulfonic acids.

The acenaphthenesulfonic acids

The reactions and compounds mentioned below are illustrated on flow-sheet C by Roman numerals.

The monosulfonic acids of acenaphthene have been the subject of much discussion and conflicting research. Since the proofs advanced for the structures of all three are to a considerable extent mutually interdependent, a brief review of the entire work will be presented here. Mention will first be made of the preparation of each sulfonic acid, and following this evidence of constitution will be presented in chronological order.

The first sulfonic acid (amide, m.p. $196-9^{\circ}$) was prepared by E. Oliveri Mandala¹⁵ and subsequently by Dziewonski²¹ by the action of concentrated sulfuric acid on the hydrocarbon at 100° .

The second sulfonic acid was first made by a commercial company¹⁶ by the action of chlorsulfonic acid on the hydrocarbon in nitrobenzene solution at $0-3^{\circ}$. The sulfonic group was thought to be on the methylene groups, but Dziewonski and Stolyhwo²¹ later showed by oxidation of the methylene groups that the sulfonic group was on the aromatic nucleus.

The third sulfonic acid was not made until after the work on structure had been completed. It will be mentioned here, and discussed later. It was prepared by Dziewonski and Orzelski²⁵ by the action of chlorsulfonic acid on 3-nitroacenaphthene in nitrobenzene solution at 0° , with subsequent removal of the nitro group. No one except Dziewonski and co-workers have prepared this acid (amide, m.p. $182-3^{\circ}$).

The first approach to the structure of these acids was based on a bromoacenaphthene prepared by Blumenthal.¹ This was prepared by the action of bromine in ether. Blumenthal showed that the bromine was on the aromatic part of the molecule by oxidation of the methylene groups. Graebe and Guinsbourg¹¹ prepared the bromo compound more easily by the action of bromine in boiling chloroform. The m.p. was given by them as 52° . Sachs and Mosebach¹³ prepared the same compound from 3-aminoacenaphthene, and reported checks in properties and a m.p. of 51.5° .

Graebe and Guinsbourg¹¹ oxidized the bromoacenaphthene by a modification of Blumenthal's method¹ to a bromonaphthalic acid, and by distilling the calcium salt with calcium hydroxide obtained alpha bromonaphthalene and some naphthalene. The bromine was, therefore, considered to have been on the 3 position of the acenaphthene originally.

The bromonaphthalic acid fused with potassium hydroxide at 290-300° (reported no reaction at 200°) gave 50% of a so-called acid anhydride of m.p. 257°, which Gaebe and Guinsbourg called 4-hydroxynaphthalic anhydride (II); and a lower melting acid not identified.

Crompton and Cyriax¹² claimed to have obtained the same compound of m.p. 257° from 3-chloroacenaphthene (m.p. 65°) by the same general reactions. It is interesting to compare the melting points of some of these compounds with those reported by Dziewonski and Zakrzewska-Baranowska²⁶ at a later date.

	S. & M. ¹³	C. & C. ¹²	Dz. ²⁶
3-chloroacenaphthene	62.5-3.0°	65.0°	69-70°
4-chloronaphthalic anhydride		198°	216-7°
4-chloronaphthalimide		278°	301-2°

E. Oliveri Mandala,¹⁵ by oxidation of the high temperature sulfonic acid (amide, m.p. 196-9°) to a sulfonated naphthalic acid, and fusion of the latter with moist potassium hydroxide at 240-50°, obtained a product of m.p. 257°, and therefore concluded that the original sulfonic acid was 3-acenaphthenesulfonic acid (No. III).

Dziewonski and Stolyhwo^{21, 22} accepted the above evidence, and advanced a proof of the structures of the sulfonic acids based chiefly on the coupling reactions of the hydroxynaphthalic acids. The first so-called hydroxynaphthalic acid (anhydride, m.p. 257°) was prepared by the reactions of Mandala,¹⁵ shown as No. III. The second was prepared by similar reactions from the sulfonic acid (amide, m.p. 222-3°) obtained by sulfonation of the hydrocarbon in nitrobenzene at 0-3°. Hydroxynaphthalic anhydride, m.p. 350-1°, reactions listed as No. IV. The third acenaphthenesulfonic acid not yet having been obtained, the corresponding hydroxynaphthalic acid was prepared by oxidizing acenaphthene to naphthalic acid, sulfonating at 90-5°, and then carrying the product through the same reactions (No. V). Hydroxynaphthalic anhydride, m.p. 287° (later changed to 280°).^{26, 28} This latter hydroxynaphthalic acid had been prepared by Anselm and Zuckmayer¹⁰ but they had not investigated the structure. Preparation of this latter hydroxynaphthalic acid was also accomplished from an aminonaphthalic acid first prepared by Anselm and Zuckmayer,¹⁰ and which Graebe¹¹ had degraded to beta naphthylamine. Reasoning on method of preparation the hydroxy group was assumed by Dziewonski and Stolyhwo to be in the 3 position (No. V).

From what is known of the positions which the diazo group enters in coupling reactions with alpha and beta naphthol, Dziewonski and Stolyhwo concluded it should enter the 3 position in the 4-hydroxy derivative, and the 4 position in the 3 derivative, whereas the 2-hydroxy derivative should

not couple at all. They found, however, that in slightly alkaline solution all three hydroxynaphthalic acids coupled with benzenediazonium chloride. Only the product from the so-called 3 derivative (anhydride, m.p. 287° , later changed to 280°)^{26, 28} was a normal coupling product (No. VI). The other two lost carbon dioxide on coupling to form dark red products easily soluble in cold alkali and insoluble in acids. If heated or simply recrystallized from organic solvents, these latter two products were converted to alkali-insoluble brick-red compounds, which could be converted again to the original alkali-soluble products by heating with aqueous alkaline solutions. This behavior was interpreted as pyridazone formation (Nos. VII and VIII). Analyses checked the expected percentage compositions.

Thus, accepting Graebe's 257° melting compound as 4-hydroxynaphthalic anhydride, the acid made by treating acenaphthene with sulfuric acid at 100° , was considered to be 3-acenaphthenesulfonic acid.

The two other hydroxynaphthalic acids were distinguished by the normal coupling as expected, of the 3 derivative, and the pyridazone formation of the 2 derivative. Therefore, from this, the sulfonic acid (amide, m.p. $222-3^{\circ}$) obtained from acenaphthene at 0° , was considered to be 1-acenaphthenesulfonic acid.

Morgan and Yarsley,²³ shortly after this, nitrated the high temperature sulfonic acid (amide, m.p. $196-9^{\circ}$), and reduced the product to an aminosulfonic acid. From this they claimed to have obtained, by diazotization, a sultone. This reaction does not occur in the benzene series, and occurs only in the naphthalene series when the groups are on adjacent peri positions. Hence it was considered a check on the positions of both of these groups (3,4 or peri). However, they reported no data to substantiate their assertion.

During the course of further work on acenaphthene, Dziewonski and co-workers²⁴ were led to believe that substitution in acenaphthene should be para to the methylene groups at low temperature and ortho to them at higher temperatures. The sulfonic acids were therefore reinvestigated.

The 3-hydroxynaphthalic anhydride was considered correctly defined (No. V). This was in view of: (a) The normal coupling of its hydroxynaphthalic acid. (b) The preparation of this hydroxynaphthalic acid from sulfonated naphthalic acid and nitrated naphthalic acid. (c) The degradation of the aminonaphthalic acid to beta naphthylamine, and the degradation of the hydroxynaphthalic acid to beta naphthol.

The low and high temperature sulfonation products were considered reversed in the former work. The reasons for believing this were as follows:

1. Graebe's ¹¹ so-called 4-hydroxynaphthalic anhydride (m.p. 257°) which had been assigned formula II, was investigated. Graebe's calculation of the empirical formula from his combustion data was shown to be in error. The combustion corresponded to $C_{10}H_6(COOH)(OH)$, not to $C_{10}H_5(CO)_2O(OH)$ or $C_{10}H_5(COOH)_2(OH)$.

2. Distillation of the calcium salt of the above acid gave only beta naphthol and not the expected alpha naphthol.

Of the four possibilities for this acid of Graebe (Nos. X, XI, XII, XIII), No. X was chosen since this acid was the one from which a phenyl pyridazone would be expected. Therefore, the sulfonic acid obtained from acenaphthene and sulfuric acid at 100°, was called 1-acenaphthenesulfonic acid.

Dziewonski and co-workers ²⁴ prepared 2-hydroxynaphthalic anhydride by the reactions listed as No. IV, using the sulfonic acid obtained from acenaphthene and sulfuric acid at 100°. They found that the potassium hydroxide fusion temperature should be kept at 150-60°. If allowed to rise to 240-50°, 2-hydroxy-8-naphthoic acid was obtained (No. X).

Later work ²⁶ on carefully purified 3-chloro and 3-bromoacenaphthene gave by the reactions listed as No. XIV, 3-hydroxynaphthalic anhydride of m.p. 280° (temperature of fusion, 220-30°). This same 3-hydroxynaphthalic anhydride was also obtained from the so-called 2-acenaphthenesulfonic acid mentioned below.²² This result was interpreted as moving of the groups during alkali fusion of the chloro compound. They reported failure to obtain Graebe's 257° melting compound from 4-chloronaphthalic anhydride at a fusion temperature of 290-300°.

The sulfonic acid formed by sulfonation of the hydrocarbon at 0-3° was considered to be 3-acenaphthenesulfonic acid. By the reactions listed as No. III, Dziewonski and co-workers ²⁴ obtained the so-called 4-hydroxynaphthalic anhydride, m.p. 350-1°. Distillation of the calcium salt with lime gave alpha naphthol.

After this work on structure had been completed, the third sulfonic acid, 2-acenaphthenesulfonic acid, was prepared for the first time ²⁵ by sulfonation of 3-nitroacenaphthene, and removing the nitro group (No. IX). Since the properties were different from the other two sulfonic acids it was considered to be 2-acenaphthenesulfonic acid with no further evidence.

In view of all this conflicting work, it seemed highly desirable to try to offer a simple proof of the structure of 3-acenaphthenesulfonic acid. This proof, it was felt, should not involve any alkali fusions or any reasoning involving coupling reactions, since it seemed that such reactions and reasoning had been the cause of much of the confusion in the former

work. Hence it was decided to try to obtain a common derivative from 3-aminoacenaphthene and 3-acenaphthenesulfonic acid. The sulfinic acid was first tried, obtaining it from the sulfonyl chloride and from the amine. However, because of its instability, this method of attack was abandoned. Attempts to oxidize the iron salt of the sulfinic acid to the sulfonamide, failed. Therefore, the sulfinic acid was oxidized with alkaline permanganate to the sulfonic acid which was converted to the methyl ester for identification. The methyl ester was chosen because of the ease of preparing it in good yield by means of methyl sulfate. The only difficulty encountered with this proof was the ease of oxidation of the methylene groups by alkaline or even neutral permanganate. By proper care, this did not cause serious trouble, since the sulfinic acid oxidized much more easily than the methylene groups. This reaction shows that the sulfonic group was on the same position as was occupied by the nitro group in the 3-nitroacenaphthene from which the amine was obtained. This checks the conclusion finally reached by Dziewonski and co-workers²⁴ concerning the position taken by the sulfonic group on sulfonation of the hydrocarbon at 0-3°.

Sodium 4,3-nitroacenaphthenesulfonate and 4,3-nitroacenaphthenesulfonyl chloride

The only report that has been found on the nitration of sodium 3-acenaphthenesulfonate occurs in a recent British patent granted to the I. G. Farbenindustrie Aktiengesellschaft.²⁷ There it is claimed that on nitration of 3-acenaphthenecarboxylic or 3-acenaphthenesulfonic acid in acetic acid solution, the nitro group enters the 4 position. An example of nitration is given on the carboxylic acid only.

It was decided by the author to prove the position of the nitro group by reducing the nitrosulfonic acid to the aminosulfonic acid, and removing the sulfonic group with sodium amalgam. This reaction, discovered by Claus² in 1877 while working on a naphthalenesulfonic acid and later applied to a series of naphthalenesulfonic acids by Friedlaender and Lucht,⁶ has been used by Dziewonski and co-workers^{21, 25} in the acenaphthene field. The proposed reactions outlined above ran smoothly yielding 3-aminoacenaphthene, thus showing that the nitro group was in the 4, or other peri position.

Attempts to prepare a methyl ester from the sodium 4,3-nitroacenaphthenesulfonate failed as did attempts to prepare the sulfonyl chloride. This latter behavior has also been noted in the naphthalene series⁸ in connection with the sodium 1,8-nitrosulfonate. Therefore, 3-acenaphthenesulfonyl chloride was prepared and nitrated.

Dziewonski and Stolyhwo²¹ had prepared 3-acenaphthenesulfonyl chloride in the crude state by the action of phosphorus pentachloride on the sodium salt, and had used this crude material for the preparation of the amide and the ethyl ester. For this research a large scale preparation of the sulfonyl chloride was developed, using phosphorus pentachloride but with quite different conditions, and the product was subsequently analyzed. The ester checked that made by Dziewonski and Stolyhwo. Dziewonski and co-workers³⁰ later purified the sulfonyl chloride and reported its melting point and properties. These agree essentially with those previously found by the author.

Nitration of 3-acenaphthenesulfonyl chloride was accomplished in acetic anhydride. This allowed lower temperatures than acetic acid without freezing, and produced less tars. Nitration in fuming nitric acid, as carried out by Bogert and Bartlett²⁹ in the naphthalene series, produced so much decomposition that no pure products were isolated from the reactions. The nitration mixture from the acetic anhydride solution contained considerable decomposition products, and two isomeric nitrosulfonyl chlorides. These were found to be not easily separated. Isolation of the desired 4,3 isomer gave only 20% yields in the pure state.

Since attempts to prepare an ester of this 4,3 isomer failed, it was decided to check the position of the nitro group by hydrolyzing the sulfonyl chloride group, and using the same reactions that had been used on the nitrosulfonic acid. Alkaline reagents could not be used because of the sensitivity of the nitro group to alkali. The sulfonyl chloride was quite stable to cold water, and boiling water gave decomposition products from which the nitrosulfonic acid was not isolated. A property similar to the latter has been noted in the naphthalene series.⁷ Therefore, the nitrosulfonyl chloride was reduced to the nitrosulfinic acid. This reaction ran very smoothly and easily. The nitrosulfinic acid was oxidized in neutral solution to the nitrosulfonic acid by means of permanganate. No difficulty was encountered. Since no derivative of the nitrosulfonic acid was available, the product was reduced to the aminosulfonic acid from which 3-aminoacenaphthene was obtained by the use of sodium amalgam. This shows that the nitro group was in the other peri position.

The position of the nitro group in the other isomeric nitrosulfonyl chloride was not determined since it was not of sufficient interest, and was not to be used in the synthetic work. The compound has been assigned a tentative structure as 5(?),3-nitroacenaphthenesulfonyl chloride since Dziewonski and Orzelski²⁵ obtained the sulfonic group in a meta position to the methylene groups on sulfonating 3-nitroacenaphthene at low temperature, and decided on the 5 position rather than the 2 position. They decided this way since the aminosulfonic acid coupled readily with diazo compounds.

It is very probable that an isomeric nitrosulfonic acid was obtained with 4,3-nitroacenaphthenesulfonic acid on nitrating sodium 3-acenaphthenesulfonate, but this acid being present in smaller amounts and being more soluble in water, was lost in the process.

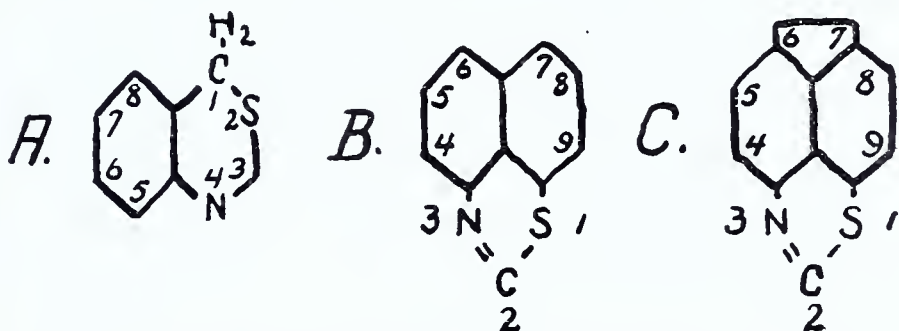
The 4,3-nitroacenaphthenesulfonyl chloride was reduced, using the method of Bogert and Bartlett²⁹ for the corresponding naphthalene compound, to the chlorostannate of the peri-aminoacenaphthenyl mercaptan from which the desired condensation products were prepared.

The fact that the nitro group in the nitrosulfonyl chloride is in a position equivalent to that of the sulfonyl chloride group, combined with the fact that ortho type condensations were made from the chlorostannate, gives a proof of the position of the original nitro group in 3-nitroacenaphthene as this is the only position in which such a combination of reactions is possible. This gives additional confirmation to the original work of Graebe and Briones¹¹ on the proof of the position of the nitro group in 3-nitroacenaphthene.

Sultone formation has not been accomplished in the benzene series, and has been accomplished in the naphthalene series only when the groups have been in the adjacent peri positions. Morgan and Yarsley,²³ using the sulfonic acid obtained from acenaphthene and sulfuric acid at 100°, have claimed sultone formation by nitration at 10°, reduction to the aminosulfonic acid, diazotizing, and boiling the product with hydrochloric acid. They advanced no experimental evidence, however. The author has obtained a sultone from 4,3-nitroacenaphthenesulfonic acid by the usual reactions.

Thiazines

The numbering of the benzometathiazine, peri-naphthothiazine, and peri-acenaphthothiazine compounds is illustrated below.



There has been considerable interest in thiazoles and in thiazole dyes since the discovery of dehydrothio-p-toluidine,³ and the introduction of Columbia Yellow as a direct cotton dye.⁵ A great deal of work has been

done in these laboratories on the various substituted benzothiazoles and on substituted Columbia Yellows. However, comparatively little work has been done on the analogous six-membered heterocycles, the metathiazines. Until a recent investigation by Bogert and Bartlett,²⁹ no dyes of the Columbia Yellow type had been prepared from metathiazines.

Investigations in the benzometathiazines have been limited to derivatives of 2,4,1-benzothiazine (Formula A) which are all yellow or colorless compounds.

Reissert¹⁸ prepared one naphthalene thiazine, the 2-phenyl-peri-naphthothiazine which forms golden yellow needles. This compound is isomeric with the 2-phenyl-naphthothiazoles.

Bogert and Bartlett²⁹ continued the work on the peri-naphthothiazines, investigating their properties and methods of preparation. They observed that ring closure in the peri position to form naphthothiazines, is in general accompanied by a marked increase in depth of color. Of the 2-(nitrophenyl)-peri-naphthothiazines the ortho isomer was orange, the meta isomer golden brown, and the para isomer cherry red. The corresponding amines were all yellow and differed but little from each other. The dyes of the Columbia Yellow type were prepared. The para isomer dyed unbleached cotton a burgundy color which in "fastness to light, laundering, and bleeding, compared well with Columbia Yellow dyeings." The meta isomer gave a tan color to cotton but was "not so fast to light, laundering, and bleeding as the para isomer." It was shown that the syntheses of the thiazines could be carried out by the reduction of 1,8-nitronaphthalenesulfonyl chloride with stannous chloride, dry hydrogen chloride, acetic acid mixture to produce a chlorostannate of the amino mercaptan which was condensed in sodium acetate, acetic acid solutions with acid chlorides.

No thiazoles or thiazines of acenaphthene have been prepared. Of related types, Sachs and Mosebach¹⁴ have prepared aceperimidine by the action of formic acid on 3,4-diaminoacenaphthene. M. Witte¹⁷ also prepared this compound which forms yellowish-brown scales easily soluble in all organic solvents. She also prepared, besides other derivatives not of interest, 2-phenyl-aceperimidin by the action of benzoyl chloride on the diamine in dry benzene solution. It formed yellow to red crystals which were not very stable, apparently undergoing decomposition or oxidation even during purification. Dibenzoyl-peri-diamino-acenaphthene, obtained as a by-product from the above reaction, formed yellowish-brown needles of considerably higher melting point, and was stable.

It was the purpose of the author to extend the investigation of the metathiazines to the acenaphthene field, by synthesizing a series of condensation products and studying their properties. This would allow a comparison of the peri-acenaphthothiazines with the peri-naphthothiazines, and would determine the effect of the acenaphthene nucleus on the Columbia Yellow type of dyes in this series.

For the synthesis of the desired condensation products, 4,3-nitro-acenaphthenesulfonyl chloride was prepared, as described above, by nitration of 3-acenaphthenesulfonyl chloride. The product was reduced to a tin salt of the amino mercaptan by the action of a solution of stannous chloride in glacial acetic acid containing dry hydrogen chloride. The nitrosulfonyl chloride dissolved readily in the reducing mixture with a rapid rise in temperature. Precipitation of the tin salt began immediately. After cooling, filtering, and washing the product with acetic acid, dry benzene, and dry ether, it was found to be quite pure. Analysis indicated that the product was a chlorostannate of the peri-aminoacenaphthenyl mercaptan. The chlorostannate was readily soluble in cold absolute ethyl alcohol. However, it was decomposed very rapidly by water.

For the condensations the chlorostannate was added to a hot solution of fused sodium acetate in acetic acid. This medium was the most satisfactory one found by Bogert and Bartlett for use with the analogous naphthalene compound. Below 90° the decomposition was very slow. At 90°, however, solution took place with simultaneous precipitation of sodium chloride. The condensations were accomplished by adding benzoyl chloride, or substituted benzoyl chlorides to this reaction mixture. With para-nitrobenzoyl chloride the mono-(p-nitrobenzoyl)-peri-amino-acenaphthenyl mercaptan precipitated immediately with the thiazine. Attempts to avoid this by varying the conditions, were only partially successful. The mono-acylated compound was a tan color. The thiazine, however, was a very deep red, the crystals being almost black. With m-nitrobenzoyl chloride a mixture of di-(m-nitrobenzoyl)-peri-amino-acenaphthenyl mercaptan and thiazine precipitated. Attempts to separate these satisfactorily met with little success. It was found to be more satisfactory to run the reaction at lower temperatures with a large excess of the acid chloride, thus producing quite pure di-(m-nitrobenzoyl)-peri-aminoacenaphthenyl mercaptan from which the thiazine could be prepared very easily by boiling with sodium acetate and acetic acid. The uncyclized product was pale yellow whereas the thiazine was orange-red.

The aminophenyl-thiazines were prepared from the nitro compounds by the action of an alcoholic solution of stannous chloride containing hydrochloric acid. The para isomer was deeper in color than the meta isomer. These amines sulfonated very readily with concentrated sulfuric

acid at 60-5°. The free sulfonic acids were very difficultly soluble in water in the presence of hydrochloric or sulfuric acids. The sodium salts in alkaline solution oxidized readily with alkaline hypochlorite to dyes of the Columbia Yellow type. However, in the presence of an appreciable excess of hypochlorite, the dyes were slowly bleached to pale yellow compounds quite insoluble in water. There was a considerable increase in weight during this action. The dyes were direct on cotton. The para isomer gave an apricot shade, the meta isomer a peach one. Both were quite stable to light and bleeding, but only moderately stable to laundering.

EXPERIMENTAL

Unless otherwise stated, all the melting points recorded below, which were taken by the author, are corrected, and all, including those which decomposed, were taken while heating the bath at the rate of 3° per minute.

1. 3-Nitroacenaphthene

This compound was prepared by the method of Sachs and Mosebach¹⁴ with a minor variation. Fifty g. of acenaphthene was dissolved in 400 cc. of glacial acetic acid by warming, and the solution was cooled quickly with good shaking. Part of the hydrocarbon separated as very small crystals. The solution was kept well stirred, and 50 cc. of nitric acid (Sp. Gr. 1.42) was slowly added over a period of twenty minutes. It was found that if the temperature was kept at 10° from the beginning, as recommended, the solution froze. Therefore, the temperature was kept at 15-8° at the beginning and was gradually lowered to 10°. After all the nitric acid had been added, the solution was allowed to stand twenty-five minutes, and the precipitated nitro compound was filtered. Yield, 47.5 g., or 74%. After two crystallizations from alcohol it melted at 103°. The m.p. recorded by Morgan and Stanley²⁰ is 106°. It was found to be easier to purify the amine than to carry purification further at this stage.

2. 3-Aminoacenaphthene

The method of Fleischer and Schranz¹⁹ was used for this preparation. Nineteen g. of 3-nitroacenaphthene was dissolved in 200 cc. of hot alcohol and 100 cc. of hot water was added. Fifty g. of commercial sodium hydrosulfite was added in portions small enough to keep the mixture from boiling too vigorously, and the solution was then boiled until practically all the color had gone. The alcohol was distilled off, and a

mixture of 100 cc. of water and 100 cc. of concentrated hydrochloric acid was added. The solution was boiled one-half hour and filtered. On adding ammonium hydroxide to the filtrate the amine precipitated. Further extraction of the acid-insoluble residue with dilute hydrochloric acid yielded more amine. The combined amine precipitates were dried. Yield, 15.3 g. The product was crystallized from ligroine and from water. The m.p. was then 107.5°. Morgan and Stanley²⁰ report 108°.

3. Sodium 3-acenaphthenesulfonate

The method used for this preparation was that of the patent by Kalle and Co.¹⁶ One hundred g. of acenaphthene was dissolved in a kilogram of dry nitrobenzene and the solution was then cooled to 0°. Seventy-eight g. of technical chlorsulfonic acid was added dropwise while the solution was kept well stirred and the temperature was kept at 0°. When all the acid had been added, the solution was allowed to warm up to 20° over a period of one-half hour. It was then poured into one liter of water, and after thorough mixing, the aqueous layer was separated. The nitrobenzene was extracted with a 100 cc. portion of water. The combined water layers, after neutralizing with sodium carbonate, were heated to boiling. The solution was stirred thoroughly while 310 g. of well ground salt was added in one portion. After cooling and filtering, the sodium salt was dissolved in 600 cc. of boiling water, filtered, and again salted out in the same manner by 144 g. of salt. The product separated as glistening white plates, which were sucked as dry as possible on the filter, and then dried at 130°. The yield averaged 153 g., or 92%.

4. Methyl 3-acenaphthenesulfonate

Five g. of sodium 3-acenaphthenesulfonate which had been dried at 130°, was heated to boiling with 20 cc. of dimethyl sulfate for ten minutes under a reflux condenser. The solution was then cooled and 100 cc. of water was added. After warming again for a few minutes, the solution was cooled and extracted with ether. The ether was allowed to stand over anhydrous sodium sulfate and anhydrous sodium carbonate until it was dry and the methyl sulfate was all decomposed. After filtering and evaporating the ether with a stream of air, the product was taken up in boiling alcohol and precipitated by hot water. Yield, 3.6 g., or 74%. On recrystallization from ligroine, and from methanol, the ester came out as long white needles of m.p. 131.0-2.0°.

Analysis

Calcd. for C ₁₃ H ₁₂ O ₃ S:	C, 62.87;	H, 4.87
Found:	C, 62.74;	H, 5.07

5. Conversion of 3-aminoacenaphthene to methyl 3-acenaphthenesulfonate

Gattermann's⁹ method for preparing sulfinic acids from amines, was used as a reference in the first step of this procedure. Three solutions were prepared. (A) Ten g. of 3-aminoacenaphthene was dissolved by heating in a mixture of 35 cc. of concentrated hydrochloric acid and 150 cc. of water. (B) 4.08 g. of sodium nitrite was dissolved in 20 cc. of water. (C) Two hundred cc. of water containing 70 g. of finely divided copper powder, was saturated with sulfur dioxide. Solution A was kept at 0-5° while solution B was added with stirring. The mixture turned bright green. This diazo solution was then poured slowly into solution C at room temperature, during which time solution C was stirred thoroughly and a rapid stream of sulfur dioxide was being bubbled in at the bottom. The sulfur dioxide was allowed to run one hour after which the solution was filtered, and the filtrate rejected. The precipitate was washed with successive portions of dilute ammonium hydroxide, totaling 1200 cc. After cooling to 5° and acidifying strongly with concentrated hydrochloric acid, the crystalline precipitate of sulfinic acid was filtered.

The sulfinic acid was oxidized immediately to sulfonic acid at room temperature. The precipitate was dissolved in a solution of 5 g. of sodium carbonate in about 150 cc. of water, and a few cc. of dilute sodium hydroxide were added. To this well stirred solution there was added dropwise, a solution of 6.3 g. of potassium permanganate in 100 cc. of water. The oxidation was instantaneous. On filtering a sample and acidifying, some free sulfinic acid precipitated. Therefore, a solution of 2 g. of potassium permanganate in 35 cc. of water was added as before. After filtering the entire solution and washing the manganese dioxide with water, the combined filtrates were evaporated to 100 cc. The sodium 3-acenaphthenesulfonate was precipitated by adding 36 g. of finely powdered salt to the well stirred hot solution. After cooling, the sodium salt was filtered, redissolved in 75 cc. of hot water, and again precipitated in the same manner by adding 22 g. of salt. The yield was 6.7 g. of shining, very pale yellow plates, when dried at 130°. This is 45%, calculated from the original amine.

For the identification of this salt, 5 g. was esterified as described in No. 4. Yield 3.5 g., or 72%, which on crystallization from ligroine and from methanol melted at 131.0-2.0°. A mixed m.p. with the ester from the sulfonic acid obtained in No. 4 by direct sulfonation of acenaphthene, showed no depression. This proves that the sulfonic group on direct

sulfonation entered the same position as did the nitro group on direct nitration of acenaphthene.

Analysis

Calcd. for $C_{13}H_{12}O_3S$:	C, 62.87;	H, 4.87
Found:	C, 62.74;	H, 4.95

6. Nitration of sodium 3-acenaphthenesulfonate

Sixty g. of sodium 3-acenaphthenesulfonate, ground to 70 mesh and dried at 130° , was nitrated in 60 cc. of glacial acetic acid using 30 cc. of pale yellow nitric acid of Sp. Gr. 1.6. The acetic acid was kept at $15-8^\circ$ at the start, and as the nitration proceeded the temperature was lowered gradually to 10° . The sodium salt was added slowly to the well stirred acetic acid, and the nitric acid was allowed to drop in slowly throughout the nitration period. After all the sodium salt and nitric acid had been added, the temperature was kept between 0° and 10° for 15 minutes. The mixture was then poured into 900 cc. of water, stirred and filtered. It was precipitated cold with 324 g. of salt, filtered, redissolved in 500 cc. of hot water, and precipitated hot by 160 g. of salt. Dried on porous plates, and then at 120° , the yield was 59.5 g., or 85%. The product, of course, contained some salt. It was a bright yellow powder which was very soluble in water. Neither a lead, barium nor silver salt was precipitated. It was not stable to alkaline conditions. All attempts to prepare an acid chloride resulted only in decomposition. For analysis the salt was crystallized from 60-70% alcohol in which saturated solutions were obtained only after long boiling.

Analysis

Calcd. for: $C_{12}H_8O_5NSNa$:	C, 47.82;	H, 2.68;	Na_2SO_4 , 23.59
Found:	C, 47.79;	H, 2.83;	Na_2SO_4 , 23.52

7. 4,3-Aminoacenaphthenesulfonic acid

Ten g. (weight corrected for presence of salt) of sodium 4,3-nitro-acenaphthenesulfonate was dissolved in 150 cc. of water and warmed with excess zinc shavings and hydrochloric acid until the solution ceased precipitating the aminosulfonic acid. The zinc used was first washed with dilute hydrochloric acid containing a few drops of copper sulfate solution. The reducing solution was filtered and the amino acid dissolved from the zinc residue by heating with excess dilute sodium bicarbonate solution containing a little sodium sulfite. The hot filtered solution on acidification with hydrochloric acid precipitated the amino acid as micro rods, slightly tan in color. The product was filtered and washed with water, alcohol and ether. Yield 4.55 g., or 55%. It was recrystallized

from water in the same way using the theoretical amount of sodium bicarbonate and acidifying in the presence of sulfur dioxide. The product was dried at 110°.

Analysis

Calcd. for: $C_{12}H_{11}O_3NS$:	C, 57.79;	H, 4.45
Found:	C, 57.80;	H, 4.70

8. 3-Aminoacenaphthene from 4,3-aminoacenaphthene-sulfonic acid

The method applied here has been used by Friedlaender and Lucht⁶ in the naphthalene series, and by Dzewonski and co-workers^{21, 25} in the acenaphthene series. Two g. of 4,3-aminoacenaphthenesulfonic acid was dissolved in 125 cc. of hot water containing one g. of sodium bicarbonate, and the solution was then cooled to room temperature and saturated with carbon dioxide. Fifty g. of freshly prepared sodium amalgam (5%) was added over a period of one hour while a steady stream of carbon dioxide was being passed through the solution. The flow of gas was continued until the amalgam was completely exhausted. This usually required 5 hours or longer. The precipitated amine was then filtered, and the filtrate was rejected. Yield, 1.1 g., or 82%. After dissolving in dilute hydrochloric acid, filtering, and precipitating with ammonium hydroxide the product was again dried. Recrystallized once from water in which it was soluble hot to the extent of about one g. per liter, and then once from a small volume of ligroine, the amine was practically white and melted at 107.5°. A mixed melting point with a known sample showed no depression. This shows that the nitro group entered the other peri position on nitration of sodium 3-acenaphthenesulfonate.

9. Peri-acenaphthsultone

Peri-acenaphthsultone was prepared by a method analogous to that used by Erdmann⁴ for the corresponding naphthalene sultone. Six and one-half g. of 4,3-aminoacenaphthenesulfonic acid was suspended in 200 cc. of water and dilute sodium hydroxide was added until solution took place. The solution was then cooled to 15°. A separate solution was made of 1.9 g. of sodium nitrite in 20 cc. of water. These two solutions were alternately added in small portions to a well stirred solution consisting of 20 cc. of concentrated hydrochloric acid and 20 cc. of water at 15°. The mixture was then stirred one-half hour at this same temperature. The slight excess of nitrite was then removed by adding urea. Fifteen cc. more of hydrochloric acid was added and the solution was heated to boiling until the nitrogen ceased being evolved. After cooling and filtering, the crystalline precipitate was dried. Yield 3.0 g., or

50%. It was crystallized first from benzene and then from alcohol, yielding long white needles of m.p. 173.0°. The sultone was not affected by cold aqueous ammonium hydroxide or sodium hydroxide. Alcoholic ammonia dissolved it slowly in the cold and much more readily when hot to a clear yellow solution. Hot aqueous sodium hydroxide dissolved it quite readily.

Analysis

Calcd. for $C_{12}H_8O_3S$:	C, 62.04;	H, 3.47;	S, 13.81
Found:	C, 62.09;	H, 3.59;	S, 13.47

10. 3-Acenaphthenesulfonyl chloride

This compound was prepared in the crude state in 1924 by Dziewonski and Stolyhwo²¹ by the action of phosphorus pentachloride upon the sodium salt. The method given below uses phosphorus pentachloride but under quite different conditions. After the author had worked out the method below, purified the compound, analyzed it, and continued with the experimental work, Dziewonski and co-workers³⁰ published an article in which they reported purification of the acid chloride, analysis and properties. The m.p. and properties as reported by them agree substantially with those given below.

One hundred fifty g. of sodium 3-acenaphthenesulfonate, ground to 70 mesh and dried at 130°, was cooled in a lightly corked balloon flask in an ice-water mixture. There was added 165 g. of ground phosphorus pentachloride at one time, and the mixture was shaken vigorously. Shortly after mixing, the reaction started, and the mixture became liquid. The temperature rose rapidly. This heat was absorbed by immersing the flask in the ice bath. The reaction was then allowed to stand slightly warm for 20 minutes, warming gently on the water bath if it started to solidify. It was then poured in a thin stream into a well stirred ice-water mixture and stirred until the product became quite granular, after which it was filtered, ground in a mortar under ice water, and again filtered and spread on porous plates to dry. Weight of crude, 128 g. The dry crude tan product was dissolved in 90-5 cc. of warm benzene and four times the volume of gas machine gasoline was added slowly with stirring. This precipitated most of the tar and extracted slightly under one-third of the acid chloride. After the tar had settled the clear liquor was decanted and evaporated to dryness by a gentle air blast. The benzene treatment was repeated three more times on the tarry residue, and each fraction was evaporated as described before. The acid chloride separated as long yellow needles of m.p. 91-100°. Yield 100 g. Further purification was done by crystallization from ligroine (b.p. 80-110°) using 7 cc. per g. The 100 g.

of crude gave 68 g. of m.p. 100° to 106° . It was found to be impractical to purify this material any further for the nitrations. For analysis a sample was crystallized from ligroine. When pure it softened at 109° and melted from 110° to 111° . Dziewonski and co-workers reported a m.p. of $109-11^{\circ}$. The product was soluble in ether, acetone, ethyl acetate, chloroform, and acetic acid. From ligroine it formed large flat yellow needles. Dziewonski and co-workers reported small colorless needles.

Analysis

Calcd. for: $C_{12}H_9O_2S$ Cl:	C, 57.01;	H, 3.59
Found:	C, 56.99;	H, 3.93

11. Ethyl 3-acenaphthenesulfonate

This ester was prepared as a check on the sulfonyl chloride and sulfonic acid. The method of Dziewonski and Stolyhwo²¹ was followed with a minor variation. Five g. of 3-acenaphthenesulfonyl chloride was boiled under a reflux condenser for 50 minutes with 75 cc. of absolute ethyl alcohol. The solution was cooled, and poured on to ice and water, whereupon the ester precipitated as fine needles. Yield, 3.9 g., or 75%. After one crystallization from ligroine the yield was 3.2 g., or 61%. Crystallized from alcohol with noriting, and from ligroine, it formed long colorless needles of m.p. $140.0-1.0^{\circ}$. Dziewonski and Stolyhwo report a m.p. of $137-9^{\circ}$.

Analysis

Calcd. for $C_{14}H_{14}O_3S$:	C, 64.07;	H, 5.38
Found:	C, 64.07;	H, 5.23

12. Nitration of 3-acenaphthenesulfonyl chloride

This nitration was done in acetic anhydride using pale yellow nitric acid of Sp. Gr. 1.5. One hundred g. of finely powdered 3-acenaphthene-sulfonyl chloride was suspended in 100 cc. of acetic anhydride, and the mixture was stirred thoroughly while 40 cc. of the nitric acid was added dropwise. The addition was made as quickly as possible, keeping the temperature at 10° . After about one-half of the nitric acid had been added, the precipitation of the nitrosulfonyl chloride necessitated further slow addition of acetic anhydride. This usually required 70 to 80 cc. The reaction was stirred for 5-10 minutes more at the end, and was then poured into a stirred ice-water mixture. The granular precipitate was filtered, washed with water, and dried on porous plates. Yield, 117 g. of light yellow product. When dry, the material was ground in a mortar with excess ether and filtered. This treatment removed much of the tar. Yield 104 g. of m.p. $120-30^{\circ}$. This impure product was found to contain the desired 4,3-nitroacenaphthenesulfonyl chloride mixed with an isomer.

The separations and purifications were far from satisfactory, but the methods given below are the only ones that were at all successful of many that were tried. The crude was first crystallized from eight times its weight of acetic acid. The acetic acid was heated on a hot plate. When the temperature reached 85-90°, all the finely ground crude was added at one time with good stirring. When the temperature reached 100° (not above), the solution was filtered quickly with suction and allowed to cool to room temperature in the suction flask. The material on the filter paper, although dark in color, was quite pure 4, 3-nitroacenaphthene-sulfonyl chloride. The cool acetic acid was quickly filtered. The product was opaque rosettes of fine needles. The combined weight of this and the material insoluble in the hot acetic acid was about 42 g. of m.p. 145° to 150°, or higher. Final purification was effected by means of chloroform freshly distilled over sulfuric acid to remove the alcohol. Thirteen g. portions of the material were extracted with 100 cc. of the chloroform in the hot extractor described below. After about 35-40 minutes the product had all dissolved leaving a small amount of black tar on the paper. On adding petrolic ether to the hot solution until it clouded heavily, the 4, 3-nitroacenaphthenesulfonyl chloride precipitated as fine very pale yellow needles which usually melted within a few degrees of an analytically pure sample.

The original acetic acid crystallization liquor on standing always deposited more crystals. If allowed to stand too long after coming to room temperature, these crystals were deposited with the main precipitate. If this latter occurred, the increased yield melted somewhat lower, and after the above chloroform treatment the product, although free of tar, also melted low. However, by dissolving the product from the chloroform in hot benzene and precipitating it by clouding the warm solution very thoroughly with petrolic ether, the resulting material melted correctly. In spite of this additional purification, the yield, calculated from the original 104 g. of crude, was always practically the same. Yield, 24 g., or 20%.

For analysis a sample was crystallized from pure chloroform free of alcohol. It formed rosettes of fine yellow needles which usually fractured on drying, leaving them white and opaque. Placed in the bath at 186°, the compound decomposed vigorously at 190.3-1.3°, when heating 6° per minute. Placed in the bath at 176°, it darkened at once, and decomposed vigorously at 189.3-90.3°, heating 10° per minute.

Analysis

Calcd. for: $C_{12}H_8O_4NSCl$:	C, 48.39;	H, 2.71;	N, 4.71
Found:	C, 48.26;	H, 2.66;	N, 4.96

The nitrosulfonyl chloride possessed the same instability toward alkali as was exhibited by the nitrosulfonic acid.

Boiling water gave decomposition but no free sulfonic acid was isolated. Efforts to esterify it failed.

The original acetic acid crystallization liquor deposited on standing 10-5 g. more of crystals which were mentioned above. This was treated with chloroform and petrolic ether in the same manner as described above for the first precipitate. The resulting product was crystallized from benzene using petrolic ether in successively smaller amounts for each crystallization as the product became more pure, until in the last crystallizations only a few drops were used to start precipitation from the benzene. The product was then crystallized from pure benzene or pure chloroform. There was obtained in this way 1.3-1.9 g. of an isomeric nitrosulfonyl chloride which melted at $167.5-8.5^{\circ}$ without decomposition. Seven or more crystallizations were necessary. The product formed pale cream-yellow needles which were much more soluble in all solvents than the 4, 3 isomer. A mixed m.p. with the 4, 3 isomer was approximately 140° .

Analysis

Calcd. for $C_{12}H_8O_4NSCl$:	C, 48.39;	H, 2.71;	N, 4.71
Found:	C, 48.59;	H, 2.68;	N, 4.94

The residues obtained by evaporation of the chloroform used for crystallization of the 4, 3 isomer yielded the same proportional amount of the low melting isomer.

The original acetic acid crystallization liquor diluted with water yielded mostly tar. After extensive washing with ether and fractionation from benzene, chloroform, and mixtures of the two with petrolic ether, an original 10 g. portion yielded 0.45 g. of the low melting isomer.

Hot Extractor

The hot extractor mentioned above consisted of a pyrex test tube 1.5x6 inches. A hole was blown in the bottom, and a tube $\frac{1}{2}$ x2 inches was fused on. This tube was made like the bottom of a reflux condenser, having a beveled bottom with a small hole in the side. The material to be extracted was placed in a Soxhlet thimble or preferably in a large suitably folded filter paper, and an Erlenmeyer flask containing the solvent was attached by means of a cork. A reflux condenser was used in the top with a cork connection. If a Soxhlet thimble was used, three thin glass rods in the appropriate shape to fit the tube vertically, were used to allow passage on the sides for the hot vapor. The rods were hook shape on the top to allow them to be hung from the top of the thimble. This extractor

gave rapid, efficient, hot extraction since the body of the tube could be wrapped in asbestos if desired. No search of the literature was made to see if this extractor was original.

13. Proof of the position of the nitro group in 4,3-nitro-acenaphthenesulfonyl chloride

Since efforts to prepare esters from the nitrosulfonyl chloride and also from the nitrosulfonic acid were unsuccessful, and since boiling the nitrosulfonyl chloride with water gave unidentified decomposition products, the proof of the position of the nitro group was done as recorded below.

Five g. of 4, 3-nitroacenaphthenesulfonyl chloride was ground in a mortar with 3.2 g. of sodium bicarbonate, and the mixture was added to 2.6 g. of anhydrous sodium sulfite dissolved in 20 cc. of water. The mixture was warmed to 30-40° until evolution of carbon dioxide began. It was allowed to stand until a clear orange-red solution was formed, occasionally washing down the sides with water and warming gently if the reaction stopped. The solution was then diluted to about 100 cc. with water and cooled to 5°. The free nitrosulfinic acid was precipitated by adding concentrated hydrochloric acid. After 15-20 minutes the sulfinic acid had digested enough to filter. The bright yellow product was washed two or three times on the filter with dilute hydrochloric acid.

The 4, 3-nitroacenaphthenesulfinic acid was oxidized at once to the nitrosulfonic acid. It was dissolved in about 100 cc. of water by adding solid sodium bicarbonate slowly until on warming no solid remained and carbon dioxide ceased coming off. A clear orange solution resulted. This was cooled to 15°, and while stirring, a solution consisting of 1.77 g. of potassium permanganate and 1.52 g. of hydrated magnesium sulfate in about 50 cc. of water, was added dropwise. The oxidation was instantaneous. When the manganese dioxide had coagulated the solution was filtered, and the manganese dioxide after being washed with water was rejected. The combined filtrates and washings which were clear yellow, contained the 4, 3-nitroacenaphthenesulfonic acid.

The nitrosulfonic acid was reduced in this same solution with zinc and hydrochloric acid to 4, 3-aminoacenaphthenesulfonic acid. This was done by making the solution strongly acid with hydrochloric acid, and adding excess zinc turnings which had been washed in a dilute hydrochloric acid solution containing a little copper sulfate. The mixture was kept warm on the water bath until practically all the color had disappeared, and no more free amino acid was precipitating. The solution was filtered and the filtrate was rejected. The zinc residue was heated with 500 cc. of water containing a little sodium bicarbonate and sodium sulfite. On filtering and acidifying the hot filtrate with hydrochloric acid, the free

aminosulfonic acid precipitated. The solution was cooled and filtered, and the precipitate was washed with water, alcohol, and ether. Yield, 2.9 g., or 70%, calculated from the original 5 g. of nitrosulfonyl chloride.

Two g. of the above 4,3-aminoacenaphthenesulfonic acid was converted to 3-aminoacenaphthene as described in No. 8. The crude amine so obtained was dissolved in hot dilute hydrochloric acid, and precipitated with ammonia. Yield, 1.15 g., or 85%. The m.p. was 105°. Recrystallized once from water, and then once from ligroine, the product melted at 107.5°. A mixed m.p. with a known sample of 3-aminoacenaphthene showed no depression. This proves that the nitro group was in the other peri position.

14. Chlorostannate 4,3-aminoacenaphthenyl mercaptan

The method used in the naphthalene field by Bogert and Bartlett,²⁹ was applied with a minor variation to this reaction. Fifty-nine g. of powdered, hydrated stannous chloride was suspended in 180 cc. of glacial acetic acid and dissolved by passing in a stream of dry hydrogen chloride. The increase in weight was usually about 20 g. Excess above this did no harm unless 24 g. or more was added. In the latter case the reaction mixture usually frothed over when the nitrosulfonyl chloride was added. To this solution there was added at one time 10 g. of finely powdered 4, 3-nitroacenaphthenesulfonyl chloride, and the reaction mixture was shaken vigorously. The material dissolved at once, and the temperature rose rapidly to about 80°. The chlorostannate precipitated as fine yellow needles which were filtered after the solution had cooled. The product was washed thoroughly with acetic acid, dry benzene and dry ether. The yield was 11.5 g., or 93%. The product was insoluble in benzene, ether, ethyl acetate, chloroform. It was soluble in absolute ethyl alcohol. Water caused immediate decomposition.

For analysis an analytically pure sample of the nitrosulfonyl chloride was reduced with a carefully filtered sample of reducing solution. The product was washed thoroughly as described above, and dried in a dessicator over sulfuric acid and paraffin.

Analysis

Calcd. for: $C_{24}H_{24}N_2S_2SnCl_6$:

C, 39.14; H, 3.29; SnO_2 , 20.48; Cl, 28.91; S, 8.72

Found:

C, 39.40; H, 3.19; SnO_2 , 20.34; Cl, 28.96; S, 8.70

15. 2-Phenyl-peri-acenaphthothiazine

The use of sodium acetate and acetic acid to decompose the chlorostannate and to act as a solution for the acid chloride condensations, has been described by Bogert and Bartlett²⁹ by whom it was used for the peri-naphthothiazines.

Five g. of the chlorostannate was added to a solution of 5 g. of sodium acetate and 50 cc. of acetic acid at 90°. The mixture was shaken at this temperature until all the chlorostannate had decomposed, forming a clear orange solution and precipitating sodium chloride. This reaction took about ten minutes. Three g. of benzoyl chloride dissolved in a few cc. of acetic acid, was added all at one time, and the mixture was shaken and allowed to stand for one hour. It was then refluxed for one and one-half hours and cooled. On filtering and washing the precipitate with a little acetic acid and then with water, there remained 0.5 g. of red needles which melted at 105°. The red filtrate was poured into water. There appeared an orange precipitate which was filtered and dried. This contained considerable tin. The combined precipitates were extracted in the hot extractor described in No. 12 until the red color had all been removed. On cooling the alcohol, 1.1 g. of long, feathery, red crystals appeared. The m.p. was 122-3°. The residue undissolved by the alcohol was tan in color and very tarry. Nothing was obtained from it. The 1.1 g. crystallized from alcohol with noriting gave 0.75 of reddish-orange needles which started to shrink at 126.5° and melted at 139-42°. After further crystallization from alcohol it began to shrink and soften at 128° and finally melted completely at 142.3°. The compound was readily soluble in alcohol, acetone, ethyl acetate, acetic acid and benzene.

Analysis

Calcd. for $C_{19}H_{13}NS$:	C, 79.39;	H, 4.56;	N, 4.88
Found:	C, 79.45;	H, 5.25;	N, 5.22
	79.49;	5.27;	

16. Condensation of the chlorostannate with m-nitrobenzoyl chloride

Five g. of the chlorostannate was added at one time to a solution of 5 g. of fused sodium acetate in 50 cc. of acetic acid at 90°. The chlorostannate dissolved in about 10 minutes to form an orange solution, and sodium chloride precipitated. Five g. of m-nitrobenzoyl chloride dissolved in about 10 cc. of acetic acid, was added with vigorous shaking over a period of 10 minutes. The reaction was allowed to stand for three-quarters of an hour at 60°, and was then cooled and filtered. The orange precipitate was washed with a little acetic acid, and then with water to remove the salt. Yield, 4.0 g. It began to shrink at 181.0°, and melted from 192.5° to 196.5° with decomposition. The product was extracted with about 100 cc. of alcohol in the hot extractor described in No. 12 until all the orange color was removed. The cooled alcohol yielded 1.2 g. of orange precipitate which started to shrink at 170.5°, and melted from

there up to 196.5° . The residue undissolved by the alcohol (2.5 g.) was yellow. It started to shrink at 196.5° and melted from there up to 202° with decomposition, turning red. Both fractions were mixtures.

After many attempts at purification, involving among other things, several crystallizations from acetic acid and acetone with noriting, the orange product was abandoned. Yield, 0.5 g. of orange needles which melted at $185-90^{\circ}$ with decomposition. This was suspected to be and was later shown to be impure 2-(m-nitrophenyl)-peri-acenaphthothiazine.

The yellow, alcohol-insoluble residue gave similar results. Mainly cellosolve and acetic acid were used for its purification which was not carried further when 0.2 g. remained. This, when placed in the bath at 225° , started to shrink, and melted with decomposition up to 230° , turning orange-red. When heated with 0.5 g. of fused sodium acetate in 8 cc. of acetic acid, it turned orange-red and dissolved quickly. After heating 15 minutes, the cooled solution deposited orange-red needles melting at about the same temperature as the abandoned sample above. It was therefore suspected that the yellow material was a di-(m-nitrobenzoyl)-peri-aminoacenaphthenyl mercaptan. This was later found to be true.

The acetic acid reaction mixture originally used for the condensation, on adding water precipitated an orange-yellow product containing much tin. Nothing was isolated from this.

17. Di-(m-nitrobenzoyl)-peri-aminoacenaphthenyl mercaptan

Five g. of the chlorostannate was decomposed as described in No. 16, in 100 cc. of acetic acid containing 5 g. of fused sodium acetate. The solution was cooled to 60° , and 6 g. of m-nitrobenzoyl chloride dissolved in 10 cc. of acetic acid, was added all at one time. The mixture was shaken vigorously and allowed to cool to room temperature. The solution was then filtered. The orange filtrate was rejected. The yellow precipitate was washed with a little acetic acid and then with water. Yield, 4.0 g., or 59%. Placed in the bath at 217° , it started to turn pink at about 222° , and melted with decomposition at $231.3-2.3^{\circ}$, turning orange-red. The product was crystallized for analysis from acetic acid with noriting. It formed long, fine yellow needles. Placed in the bath at 233° , it started to turn pink at once, and completely decomposed at about 235.5° . The product was insoluble both in concentrated hydrochloric acid and in sodium hydroxide solutions. It was soluble in concentrated sulfuric acid with the production of a yellow color and was precipitated by dilution with water. It was quite insoluble in hot alcohol, but dissolved in hot ethyl acetate and in acetone.

Analysis

Calcd. for $C_{26}H_{17}O_6N_3S$: C, 62.50; H, 3.43
Found: C, 62.67; H, 3.57

18. 2-(m-nitrophenyl)-peri-acenaphthothiazine

This thiazine was always formed in varying proportions in all the condensations of the chlorostannate that were tried with m-nitrobenzoyl chloride. However, it was found to be practically impossible to isolate it in the pure state with any satisfactory yield by any of the methods tried. Therefore it was prepared by heating the diacylated compound with fused sodium acetate and acetic acid. This reaction was used in the naphthalene field by Bogert and Bartlett.

Five g. of di-(m-nitrobenzoyl)-peri-aminoacenaphthenyl mercaptan was refluxed for three-quarters of an hour with 200 cc. of acetic acid containing 20 g. of fused sodium acetate. The material dissolved in less than five minutes with the production of a deep orange-red color. On cooling, the 2-(m-nitrophenyl)-peri-acenaphthothiazine crystallized. It was filtered and washed with a little water. The product was crystallized from small volumes of acetone with no niting. Yield, 2.0 g., or 60%. It formed orange-red, long, glistening, flat needles. Placed in the bath at 183° , it melted with decomposition at $190.3-1.3^\circ$, shrinking a degree below this temperature. It was slightly soluble in alcohol, and easily soluble in ethyl acetate, acetone and acetic acid.

Analysis

Calcd. for: $C_{19}H_{12}O_2N_2S$: C, 68.63; H, 3.64; N, 8.44
Found: C, 68.72; H, 3.74; N, 8.59

19. 2-(m-aminophenyl)-peri-acenaphthothiazine

Two g. of 2-(m-nitrophenyl)-peri-acenaphthothiazine was refluxed for two hours with 5.5 g. of hydrated stannous chloride dissolved in a mixture of 200 cc. of alcohol and 12 cc. of concentrated hydrochloric acid. The deep red solution was poured into water, made strongly alkaline with sodium hydroxide, and allowed to stand one-half hour. The solution was filtered, and the precipitate was dried. The product was dissolved in hot alcohol and filtered from the insoluble residue. The solution was then nitrated and filtered. On clouding the hot solution with hot water, the amine began to precipitate. The cooled solution was filtered. Yield, 1.2 g., or 66%. It was recrystallized from water-alcohol mixtures. It formed orange-yellow needles which when placed in the bath at 165° , darkened, and finally melted at $176.7-7.7^\circ$ with decomposition. The amine was soluble in methyl alcohol, acetone, ethyl

acetate, and benzene. It dissolved only very slightly in concentrated hydrochloric acid, giving a pale violet color. In concentrated sulfuric acid it dissolved with a deep violet color. On adding water it was partly precipitated.

Analysis

Calcd. for: $C_{19}H_{14}N_2S$:	C, 75.45;	H, 4.67
Found:	C, 75.03;	H, 4.78

20. Condensation of the chlorostannate with p-nitrobenzoyl chloride

Five g. of the chlorostannate was decomposed with 5 g. of fused sodium acetate and 50 cc. of acetic acid as described in No. 16. To this solution at 90° there was added at one time 3.7 g. of powdered p-nitrobenzoyl chloride. The solution was shaken vigorously and then refluxed for two hours and cooled. On filtering and washing the precipitate with a little acetic acid and then with water, there remained 2.8 g. of dark brown material which melted at approximately $221-2^\circ$ with decomposition, turning dark red. This product was extracted with 100 cc. of ethyl acetate in the hot extractor described in No. 12 until the red color was all removed.

The residue undissolved by the ethyl acetate weighed 1.1 g. It melted at about 229.3° with decomposition, turning dark red. Recrystallization from cellosolve gave 0.7 g. of mono-(p-nitrobenzoyl)-peri-acenaphthenyl mercaptan. Purification for analysis was accomplished from the same solvent with noriting. The product formed light brown, micro needles which when placed in the bath at 245° , decomposed at $246.0-7.0^\circ$, turning dark red. The product was insoluble in sodium hydroxide and in concentrated hydrochloric acid. It dissolved in concentrated sulfuric acid to form a yellow solution and was precipitated on dilution with water. It was only slightly soluble in hot ethyl acetate, but in the presence of the thiazine it dissolved sufficiently to make the separation of the pure thiazine very difficult. It was slightly soluble in hot acetic acid.

Analysis

Calcd. for: $C_{19}H_{14}O_3N_2S$:	C, 65.11;	H, 4.03;	N, 7.82
Found:	C, 65.51;	H, 3.94;	N, 8.07

2-(p-nitrophenyl)-peri-acenaphthothiazine was isolated from the ethyl acetate, the cellosolve crystallization liquors, and from the acetic acid used in the original condensation. The ethyl acetate extraction solution containing some precipitate, was cooled and filtered. It yielded 1.1 g. of greenish material which melted at about 232° with decomposi-

tion. Evaporation of the cellosolve liquors to small volume yielded 0.3 g. of the same material of slightly better purity. Dilution of the original acetic acid reaction solution with water gave a precipitate of chocolate color. This contained considerable tin. Extraction with the same ethyl acetate used above, gave 0.25 g. more of crude thiazine of about the same purity as the 1.1 g. These three combined precipitates were refluxed with 200 cc. of ethyl acetate. The filtered solution deposited on cooling 0.3 g. of thiazine. The insoluble residue was again heated with the same ethyl acetate, filtered, and cooled. This was repeated until the thiazine was all removed from the product. Yield, 1.1 g. By this method separation could be accomplished, but if the material was extracted in the hot extractor the monoacylated product could not be separated. Using enough solvent to dissolve all the thiazine, gave very low recovery. The thiazine was then crystallized for analysis from ethyl acetate in the normal manner with noriting. Considerable refluxing was necessary to obtain hot saturated solutions. The thiazine formed long shining needles which were almost black. The solutions were dark red. It was moderately soluble in hot acetic acid but no separations could be accomplished from this solvent. It dissolved only slightly in hot alcohol. Placed in the bath at 244° , it decomposed at 253.7° , filling the tube with dark colored decomposition products.

Analysis

Calcd. for: $C_{19}H_{12}O_2N_2S$:	C, 68.63;	H, 3.64;	N, 8.44
Found:	C, 68.80;	H, 3.55;	N, 8.38

21. 2-(p-nitrophenyl)-peri-acenaphthothiazine

This condensation was done in order to try to increase the yield of p-nitrophenyl thiazine, and avoid, if possible, the formation of the monoacylated product. It was only partly successful.

Five g. of the chlorostannate was decomposed as described in No. 16, in a solution of 100 cc. of acetic acid containing 5 g. of fused sodium acetate. After cooling to 60° , 6 g. of p-nitrobenzoyl chloride dissolved in about 15 cc. of hot acetic acid, was added all at one time. The solution was shaken vigorously and allowed to cool. The pale tan precipitate was filtered, washed with a little acetic acid, and then with water, and then with a little acetic acid. It was then suspended in a solution of 200 cc. of acetic acid containing 20 g. of fused sodium acetate, and the mixture was refluxed for three hours. Gradual solution took place with the formation of a deep red color and precipitation of crude thiazine. On cooling, filtering, and washing the precipitate with a little acetic acid, there was obtained 2.25 g. of greenish black crystals which melted with decompo-

sition at about 243°. By repeated treatment with a 250 cc. portion of ethyl acetate as described in No. 20, 1.1 g. of 2-(p-nitrophenyl)-peri-acenaphthothiazine was obtained. This melted within two or three degrees of an analytical sample.

It was subsequently found that the 2-(p-aminophenyl)-peri-acenaphthothiazine could be prepared satisfactorily from the material no more impure than the above 2.25 g. The monoacylated product apparently hydrolyzed giving the aminothiophenol which caused no serious difficulty in the purification of the amine.

22. 2-(p-aminophenyl)-peri-acenaphthothiazine

Two g. of 2-(p-nitrophenyl)-peri-acenaphthothiazine was refluxed for three hours with 8 g. of hydrated stannous chloride, 10 g. of mossy tin, 30 cc. of concentrated hydrochloric acid, and 600 cc. of alcohol. A clear red solution resulted. This was decanted from the undissolved tin into a large volume of water, and the solution was made strongly alkaline with sodium hydroxide. After one-half hour the solution was filtered, and the crude amine was washed with water and dried. The product was dissolved in hot alcohol and the solution was filtered from the insoluble residue, norited, and again filtered. The hot solution was diluted with hot water to cloudiness. On cooling the amine separated. Yield, 1.3 g., or 72%. It was crystallized from water-alcohol mixtures. The amine formed orange needles which when placed in the bath at 208° gradually darkened, and melted with decomposition at 214.8-5.8°. It was soluble in methyl alcohol, acetone, ethyl acetate, and benzene. It dissolved only very slightly in concentrated hydrochloric acid to give a pale violet color. In concentrated sulfuric acid it dissolved to give a deep violet color, and was partly precipitated by adding water.

Analysis

Calcd. for: C ₁₉ H ₁₄ N ₂ S:	C, 75.45;	H, 4.67;	S, 10.61
Found:	C, 75.26;	H, 4.36;	S, 10.75

23. Dye of the Columbia Yellow type from 2-(m-aminophenyl)-peri-acenaphthothiazine

One g. of the amine was added to 30 cc. of concentrated sulfuric acid. It dissolved with the production of an intense permanganate color. The solution was heated for ten minutes at 60-5°. The color gradually turned to a deep wine red. The cooled acid was poured on to ice, producing a flocculent orange precipitate. This was filtered and redissolved in dilute sodium carbonate. No insoluble residue was found. The hot solution was acidified with hydrochloric acid and allowed to cool. It was then filtered, and the precipitate was dried. Yield, 1.3 g. of dark brown powder. This was dissolved in 250 cc. of hot, very dilute sodium

hydroxide, cooled to room temperature, and oxidized by adding 3.0 cc. of 1.23 N sodium hypochlorite. After standing five hours, the solution was heated, and about an equal volume of hot, filtered, saturated salt solution was added. The dye came out as a dark brown flocculent precipitate. The cool solution was filtered, and the dye was dissolved in hot water. The solution was filtered, and the dye was again precipitated in the same manner. It was dried by washing with alcohol and ether. The dye was insoluble in concentrated sodium hydroxide. It dissolved in concentrated sulfuric acid with the production of a port wine color. It was unstable to prolonged excess of alkaline hypochlorite, being bleached to a light yellow color, taking on a marked increase in weight, and becoming quite insoluble in water. The dye gave a tan color to unmordanted, unbleached cotton. The dyeing was fast to light and bleeding but was only moderately fast to laundering.

The dyeings with this dye and the para isomer were carried out with the following quantities of material:

2.5 g. of unbleached cotton.

50 cc. of 0.1% dye solution.

62 cc. of water.

10 drops of 10% sodium carbonate.

37 cc. of 1% sodium chloride solution.

The samples were heated for one-half hour at a temperature just below the boiling point.

24. Dye of the Columbia Yellow type from 2-(p-aminophenyl)-peri-acenaphthothiazine

One g. of the amine was sulfonated in the same manner as described for the meta amino product in No. 23. The permanganate color in the sulfuric acid gradually turned to a deep crimson red. No unsulfonated amine was found. The aminosulfonic acid was henna in color while wet and dark brown when dry. Yield, 1.3 g. This was oxidized in 250 cc. of very dilute sodium hydroxide with 3.0 cc. of 1.23 N sodium hypochlorite. It was found necessary to keep a very slight excess of hypochlorite in the solution for two hours. After five hours the solution was heated, and the dye salted out and treated as in No. 23. It formed a brown powder, slightly darker than the meta dye. It was insoluble in concentrated sodium hydroxide, and soluble in concentrated sulfuric acid with a somewhat darker port wine shade than was given by the meta isomer. With prolonged, appreciable excess of alkaline hypochlorite, the dye behaved similarly to the meta isomer. It dyed unmordanted, unbleached cotton an apricot color. The dyeing was stable to light and bleeding, but was only moderately fast to laundering.

RESULTS AND CONCLUSIONS

1. A new method of proof of structure in the acenaphthene field with respect to the sulfonic acids, has been introduced. This method avoids the alkali fusions and coupling reactions which have caused most of the confusion in the field, and definitely establishes that the position taken by the sulfonic group on low temperature sulfonation is the same position as that taken by the nitro group on low temperature nitration of acenaphthene. This substantiates the conclusions of Dziewonski, Galitzerowna, and Kocwa.²⁴

2. The position of the nitro group in 4,3-nitroacenaphthenesulfonic acid, has been definitely established. This confirms the claim made in the patent of the I. G. Farbenindustrie Aktiengesellschaft.²⁷ The position of the nitro group in 4,3-nitroacenaphthenesulfonyl chloride has been definitely established.

3. The fact that the nitro group in 4,3-nitroacenaphthenesulfonyl chloride has entered a position equivalent to that of the sulfonylchloride group, combined with the fact that the reduction product of the 4,3-nitro-sulfonyl chloride gives ortho type condensations, shows that the original nitro group in 3-nitroacenaphthene was in the peri position. This substantiates the work of Graebe and Briones¹¹ upon which much of the proof of structure in the acenaphthene field has been based.

4. It has been shown that the nitration of 3-acenaphthenesulfonyl chloride under the conditions used, produces a second isomer. Because the position of the nitro group in this isomer was not of sufficient interest in this work, it has not been investigated further.

5. Sultone formation has been accomplished in the peri positions of acenaphthene.

6. The methods of cyclization used by Bogert and Bartlett²⁹ in the peri-naphthothiazine series, have been extended to the peri-acenaphthothiazines.

7. It has been found that peri-acenaphthothiazine cyclization is accompanied by marked increase in depth of color. This is similar to results in the peri-naphthothiazines.

8. The solubilities of the thiazines have been found to be greater, in all the solvents tried, than the solubilities of the uncyclized products. This is similar to results in the naphthalene field.²⁹

9. The Columbia Yellow type of dyes, dyed cotton in shades not markedly different from the corresponding naphthalene dyes. The dye from 2-(m-aminophenyl)-peri-acenaphthothiazine dyed unmordanted, unbleached cotton a peach color, while the para isomer gave an apricot color. In regard to fastness to light, the dyeings compared well with

Columbia Yellow and the naphthothiazine Columbia Yellows. The dyes were more stable to bleeding than the naphthothiazine colors, comparing favorably with Columbia Yellow itself. In respect to laundering, the dyeings were not so fast as Columbia Yellow but were closely comparable to the naphthothiazine colors. The dyes were not stable to prolonged excess of alkaline hypochlorite, being gradually bleached, and thereby forming products which took on a marked increase in weight and which were much less soluble in water.

10. The following new compounds were prepared during the course of this work:

- (a) Methyl 3-acenaphthenesulfonate.
- (b) 4,3-nitroacenaphthenesulfonyl chloride.
- (c) 5(?),3-nitroacenaphthenesulfonyl chloride.
- (d) Peri-acenaphthsultone.
- (e) Chlorostannate of peri-aminoacenaphthenyl mercaptan.
- (f) 2-phenyl-peri-acenaphthothiazine.
- (g) Di-(m-nitrobenzoyl)-peri-acenaphthenyl mercaptan.
- (h) 2-(m-nitrophenyl)-peri-acenaphthothiazine.
- (i) 2-(m-aminophenyl)-peri-acenaphthothiazine.
- (j) Mono-(p-nitrobenzoyl)-peri-aminoacenaphthenyl mercaptan.
- (k) 2-(p-nitrophenyl)-peri-acenaphthothiazine.
- (l) 2-(p-aminophenyl)-peri-acenaphthothiazine.

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